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Early stage sustainability evaluation of new, nanoscale cathode materials for Li-ion batteries

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Abstract: We present results of early stage sustainability evaluation of two development strategies for new, nano-scale cathode materials for Li-ion batteries: (i) a new production pathway of existing material ($LiCoO_2$), and (ii) a new nanomaterial ($LiMnPO_4$). Nano-$LiCoO_2$ was synthesized via a single source precursor route at lower temperature with a shorter reaction time, resulting in a smaller grain size and, thereby, a better diffusivity for Li-ions. Nano-$LiMnPO_4$ was synthesized via a wet chemical method. The sustainability potential of these materials has then been investigated (at the laboratory and pilot production scales). The results show that the environmental impact of nano-$LiMnPO_4$ is lower compared to the other examined nanomaterial by several factors, and this regardless of the indicator for the comparison. In contrast to commercial cathode materials, this new material shows, particularly on an energy and capacity basis, results in the same order of magnitude as those of lithium manganese oxide ($LiMn_2O_4$), and only slightly higher values than those for lithium iron phosphate ($LiFePO_4$); values that are clearly lower than those for high-temperature $LiCoO_2$.

Introduction

Batteries transform chemical energy into electricity with the support of electrochemical cells. Based on their reversibility (due to the use different materials for the electrodes and electrolyte), two types of battery can be distinguished: non-rechargeable (primary) and rechargeable (secondary).[1] According to Eurostat, the statistical service of the European Commission, six different types of non-rechargeable batteries (i.e. zinc, alkaline, button alkaline, silver zinc, button zinc, lithium), and eleven types of rechargeable batteries (i.e. nickel-cadmium, nickel metal hydride (NiMH), lithium-ion, lithium-ion polymer, alkaline, chargeable titanium, lead-acid, lead traction, lead stationary, nickel-iron, nickel-zinc) are distinguished.[2]

Within the rechargeable category, lithium-Ion (Li-ion) batteries represent a particularly interesting technology due to their material-specific properties, showing simultaneously a high energy density in Wh/kg and Wh/l. These light and small batteries are therefore ideal for use as an energy supply in, for example, the small, mobile devices of information and communication technology (ICT) or electric mobility. By comparison, other commonly used secondary batteries, such as nickel-cadmium, NiMH or lead-acid batteries, exhibit inferior energy storage capabilities – explaining to a large extend their ever-diminishing relevance on the batteries market.[3]

Li-ion batteries are characterized by the fact that both electrodes are usually made of lithium intercalation compounds, which allows lithium ions to be exchanged between the two electrodes. For the positive electrode, lithium cobalt oxide ($LiCoO_2$ = LCO) is the most commonly used material.[1] However, due to the high costs and high toxicity of cobalt, the search for effective alternative Li compounds is of high importance for industry, and a variety of alterative cathode materials have been trialed in recent years, e.g. layered $LiNi_xMn_yCo_zO_2$ (so-called Li-NMC) cathodes.[4] However, as the testing and application of alternative cathode materials is typically a costly activity for industry (e.g. due to changes in production lines) it is important that comprehensive evaluations of potential cathode material alternatives are undertaken as early as possible in the development cycle and that these address not only technical performance but also product sustainability.

Here, we present the results of an early stage sustainability evaluation of alternative cathode materials for Li-ion batteries that are currently in development. Classical material production activities in the laboratory for new, nano-scaled electrode materials to be used in Li-ion batteries were combined and amended from a very early development stage and evaluated from a sustainability perspective using the Life Cycle Assessment (LCA) framework. LCA is seen currently as the most established and best developed tool for assessing the sustainability of new materials and technologies.[5] LCA comprises a comprehensive framework for quantifying the potential ecological and human health impacts of a product or system over its complete life cycle. The roots of LCA can be found in the energy-related research of the 1960s and pollution prevention, initiated formally in the 1970s.[6] LCA has been applied by a variety of different actors, including governmental organisations and a wide range of industries, with or without support from specialized research institutes and/or consulting companies. A prominent reason for this wide application is the clear guidance of international LCA standards, ISO 14'040 and 14'044.[7-8] LCA is not "site-specific", like risk assessment or EIA for instance. Hence, it is therefore more suitable for assessing early development stage products, such as the here examined new cathode materials for Li-ion batteries.

In the framework of this study here, the following two different production strategies are evaluated:

(1) **new production pathway** for synthesizing a nano-sized form of a **currently in use cathode material** (i.e. LCO) that is comparatively simpler than conventional production, using lower temperatures and with a shorter reaction time to produce a material with a smaller grain size, and

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       Supporting information for this article is given via a link at the end of the document.

(2) **development of a completely new material**, LiMnPO₄ (LMP), with a high structural stability in its nano-form for the application in Li-ion battery cathodes.

These materials have a better Li-ion diffusivity compared to conventional materials due to the smaller grain size. For instance, LMP in combination with carbon black could lead to a capacity that is up to 20% higher than for commercially used lithium iron phosphate (LFP).[9-11]

LCA of the respective production processes for the two nanomaterials here investigated (i.e. LMP and LCO) was performed at two scales: a) laboratory scale and b) an "upscaled" theoretical pilot production line. Based on a comparison with established, commercially-available cathode materials used in Li-ion batteries, the results of the LCA are then used to establish a first sustainability evaluation of an application of these new materials. The results of this type of evaluation are of a particular interest in view of current energy discussions, which are increasing focused on the potential for local and short-time energy storage solutions.[12]

These sustainability evaluations will enable a first estimation of the sustainability of these two different production strategies and a first opportunity to identify areas where material and energy flows can be optimized to enhance (ecological) sustainability. Such an evaluation is important for battery producers to ensure sustainability of their further product development. Details of the laboratory-scale synthesis of the investigated materials are provided elsewhere. [11]

Experimental Section

Today's rechargeable Li-ion batteries typically use the so-called high-temperature form of LiCoO₂ (HT-LCO) as a positive electrode material.[10,13] Currently, HT-LCO is produced mainly by stirring and heating a solid state mix (of carbonates and oxides) between 600 and 900°C for several hours in an oxidant atmosphere.[10] This process is considered as being rather energy intensive and also results in the formation of micrometric particles. However, the obtained high temperature phase of LiCoO₂ shows good electrochemical properties (a low self-discharge rate and stable cycling properties) for use as a cathode material, while the low temperature form appears to possess weaker electrochemical properties.[13]

Strategy 1 – new production pathway for LiCoO₂

Nano-sized particles of LCO, obtained via a new pathway, showed improved properties as, due to the smaller grains, they have a higher Li-ion diffusivity and consequently a higher reversible capacity.[10] The precursors used for the formation of these nano-sized particles of LCO are Li-alkoxides and/or aryloxides, tetrahydrofurane (THF), methanol, and cobalt chloride (a source of cobalt ions). THF and methanol are both used as solvents and ligands within this process. A variety of different Li-alkoxides and/or aryloxides have been used as a starting material at the lab scale (an overview of all used starting materials can be found in Table S.1 of the Supporting Information). Here, only the pathway with Li-methoxide as a starting material is considered further. Li-methoxide is considered the most promising of all the examined starting materials due to its economic advantages (e.g. lowest costs and

decomposition temperature) and low carbon content. The synthesis reaction of LCO is shown below:
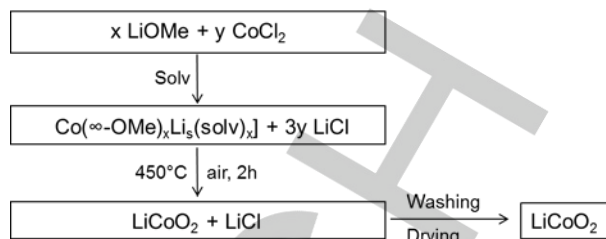
Scheme 1. Reaction scheme of the new production pathway for LiCoO₂.

The synthesis consists of the addition of the Li-methoxide to a THF-solution of CoCl₂ under Ar or N₂. This suspension was heated for 30 min under reflux followed by removal of solvent by evaporation. The obtained powder was thermally decomposed in air at 450°C and annealed at 600°C in an oven under air flux. The total production time via this new production pathway is less than 6h (compared to 36h for the solid state reaction at 850-900°C). Finally, the obtained black powder was washed several times with water and then dried with ethanol under vacuum conditions. The complete synthesis procedure for this new cathode material is described in more detail in Brog et al.[9]

Strategy 2 – new cathode material (nano-LiMnPO₄)

The second cathode nanomaterial, LiMnPO₄ (LMP), is obtained through thermal decomposition. The precursors of LMP in this process were LiOH H₂O, Mn(CH₃COO)₂ 4H₂O and H₃PO₄. Benzyl ether ((C₆H₅CH₂)₂O) was used as a solvent and oleic acid (C₁₈H₃₄O₂) and oleylamine (C₁₈H₃₅NH₂) were used as surfactants. The synthetic process of LiMnPO₄ is shown below in Scheme 2. The synthesis reaction occurred at temperatures of between 120 and 260 °C for 4-5 hours. The obtained material was rinsed with hexane and ethanol to remove the organics before the remaining surfactants of oleic acid and oleylamine were removed by ligand exchange at 70 - 80 °C.
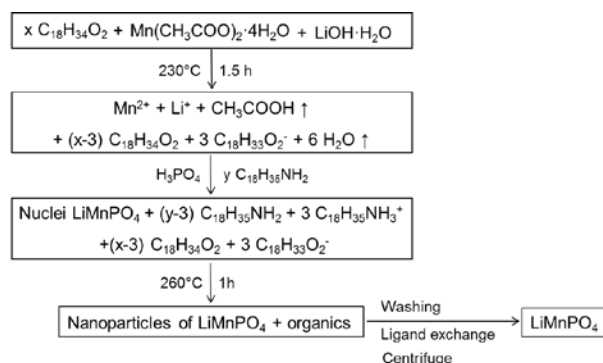
Scheme 2. Synthetic reaction scheme of LiMnPO₄ via thermal decomposition.

LMP nanoparticles were obtained in various shapes, including elongated spheres, thin rods, thick rods, needles and cubes. The sizes and the shapes of LMP nanoparticles varied depending on the synthesis temperature and the ratio of surfactants and precursors. The complete synthesis procedure

for this new cathode material is described in more detail in Kwon et al.[11]

Electrode preparation with LiCoO$_2$ and LiMnPO$_4$
Both, LCO and LMP were ball milled with carbon to produce a homogenous composite powder. Pastes were subsequently prepared by mixing this powder with polyvinylidene fluoride (PVDF) binder and N-methyl-2-pyrrolidone (NMP) solvent. The pastes were then deposited onto aluminum foil (used as current collector) to produce the two different types of cathodes. More detailed information is presented in Kwon and Fromm [14].

Life Cycle Assessment calculations
The LCA was performed using the software tool OpenLCA and with background life cycle inventory (LCI) data taken from v3.3 of the ecoinvent database[15], using the system model "allocation based on recycled-content". For those background materials for which the ecoinvent database does not contain any specific data, relevant existing datasets were chosen as proxies or new rough, gate-to-gate datasets were established (details in the electronic supplementary information). For the step of Life Cycle Impact Assessment (LCIA), one of the most up-to-date methods in this area – the ReCiPe method[16], as implemented by ecoinvent in its database version 3.3 – was applied. The large choice of impact categories in this method ensures fulfillment of the requirements of the ISO 14'040 and 14'044 standards[7-8], which require that impact categories are selected such that a broad set of environmental issues related to the product system being studied are taken into account and with due consideration for the goal and scope of the study. Here, the following assessment factors are reported, having been identified as relevant in a detailed analysis of the normalized results on the level of the lab-scale production processes: Fossil Fuel Depletion Potential (FDP), Metal Resource Depletion Potential (MDP), Global Warming Potential (GWP), Terrestrial Acidification Potential (TAP), Freshwater Eutrophication Potential (FEP), Particulate Matter Formation Potential (PMFP), Photochemical Oxidation Formation Potential (POFP), Human Toxicity Potential (HTP), Freshwater Ecotoxicity Potential (FETP), and Marine Ecotoxicity Potential (METP).

Results

LCA results of lab-scale experiments
An amount of "1 kg of produced cathode" is used as reference flow and the so-called functional unit for all the LCA calculations at the lab scale. The examined lab scale system includes all related production steps, from the extraction of the resources that are required up to the produced cathode; it is therefore an example of a so-called cradle-to-gate LCA study. As shown in Figure 1, the examined system can be split into three distinct processes on the level of this cathode production. The main data source for the three laboratory process steps shown in Figure 1 are measured data and calculations from the experimental work of these authors. These data have been complemented with information taken from the literature in order to model each single process step in a consistent and comprehensive manner. A more detailed overview of this modelling of the lab-scale experiments, together with the applied data, can be found in Section 1 of the supporting information.
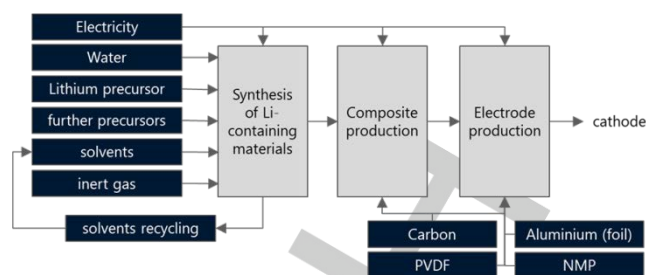

Figure 1. System boundaries of the LCA of the Lab-Scale production for the new cathode materials (dark elements are modelled with background LCI data, bright elements with data from own experiments).

When assessing now the examined production process on the level of the last process step – i.e. the actual cathode production – both examined materials, i.e. LCO and LMP, show similar results, with: all impact categories clearly dominated by the impacts from the production of the Li-containing material (as shown in Figure 2 for the case of the nano-structured LCO; the absolute values behind this figure can be found in section 4 of the supporting information).
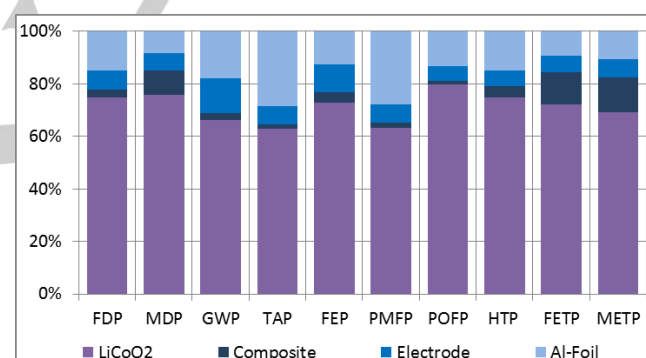

Figure 2. LCA results of 1 kg of cathode in case of the nano-structured LiCoO$_2$. Shown are results for the ReCiPe categories Fossil Fuel Depletion Potential (FDP), Metal Resource Depletion Potential (MDP), Global Warming Potential (GWP), Terrestrial Acidification Potential (TAP), Freshwater Eutrophication Potential (FEP), Particulate Matter Formation Potential (PMFP), Photo-chemical Oxidation Formation Potential (POFP), Human Toxicity Potential (HTP), Freshwater Ecotoxicity Potential (FETP) as well as Marine Ecotoxicity Potential (METP), respectively.

Figure 3 (on the next page) shows the impacts related to the production of the LCO and LMP nanomaterials (again, the absolute values behind this Figure can be found in Section 4 of the supporting information). It can be seen that, apart from the respective raw materials, two further elements dominate the contributions to the various impact categories, namely the consumption of solvents and the inert gas in the case of LCO and the solvents and the energy consumption in the case of LMP. This is a rather typical observation at the lab scale (see e.g. Piccinno and co-workers[17]) as the objective of this level being *a priori* simply the proof that a process actually works. At this stage in the material development cycle, optimization measures concerning e.g. energy consumption, use of input materials or the use of solvents and further process-related auxiliaries are not yet applied. The process of solvent recycling results partly in negative values due to the fact that the disposal

process generates small amounts of energy (electricity and heat), for which "credits" are given (more details in Section 3.7 of the supporting information).

LCA estimation of a (future) pilot production

Based on the lab-scale data, as second step an upscaling to a (calculated, theoretical) pilot production of the new LCO and LMP nanomaterials was established. The functional unit and system boundaries are consistent with those of the lab scale study. For the upscaling activity, the following general rules were applied in order to estimate higher and lower values:

- Starting materials: as lower value a yield (i.e. the amount of starting material contained within the final product) of 95% was assumed, for cobalt chloride even 98%[18]. The higher value assumes a yield of only 90% (and for cobalt chloride 95%);

- Water: reductions of 80% and 60% compared to lab scale usages were assumed for process water and cooling water, respectively;
- Electricity consumption: The lower values were calculated according to the engineering-based procedure described in the publication of Piccinno and co-workers[20] (calculations behind these values are shown in detail in the supporting information), while for the higher value this amount has been multiplied by a factor of 2.5;
- Heat consumption: the value reported represents the energy required to recover the used solvents in an internal distillation process[20];
- Waste treatment: all excess input materials are assumed to end up in an appropriate waste treatment process[19];
- Releases into air: all gases from the decomposed solvents and inert gases are assumed to be emitted into the air[20].
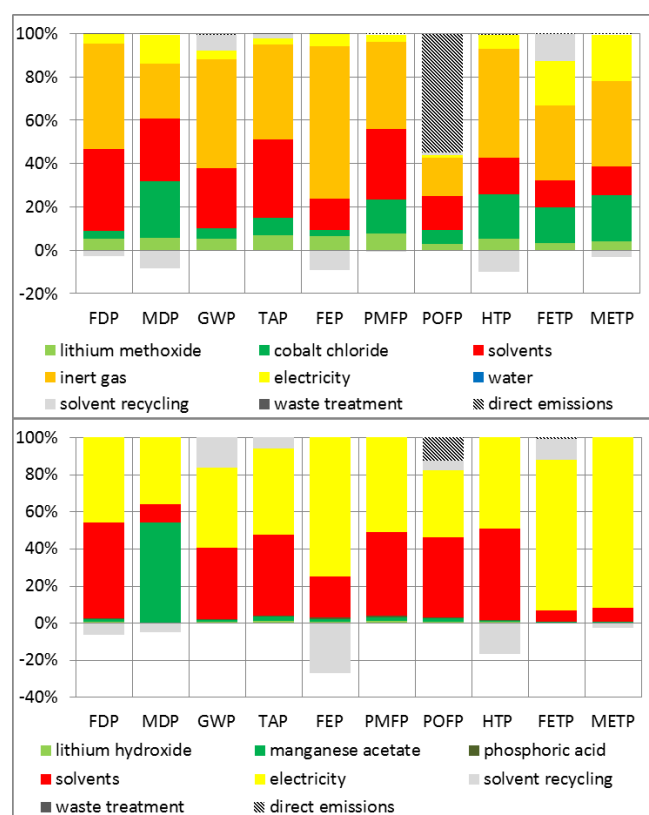

Figure 3. LCA results for the lab-scale production of 1 kg of LCO nanomaterial (upper figure) and of 1 kg of LMP nanomaterial (lower figure). Shown are the same impact categories as in Figure 2.

Figure 4. LCA results for a (theoretical) pilot production of 1 kg of LCO nanomaterial (upper figure) and of 1 kg of LMP nanomaterial (lower figure), using the lower values for the various inputs and outputs. Shown are the same impact categories as in Figure 2.

- Solvents: to minimize the use of solvents, a closed system in combination with a recycling unit (via a distillation process[19]) was modelled. It was assumed that such a closed system can be operated with 80% (higer value) to 90% (lower value) less solvent than on the lab scale;
- Inert gas: as lower value a reduction to 40% of lab scale usage, as well as an abandon of the use of multiple gases in the process, was assumed based on these authors' expert judgement. For the higher value, a 25% higher consumption (equals to a reduction to 50% of lab scale usage only) was investigated;
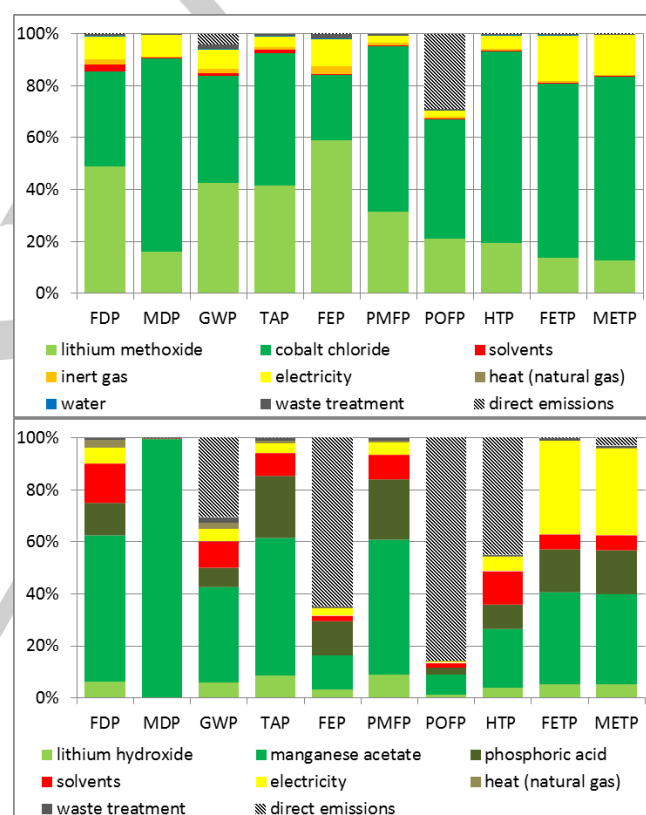
An overview of the resulting data for the pilot production of the new LCO and LMP nanomaterials can be found in Chapter 2 of the supporting information. Figure 4 shows the environmental impacts for the production of 1 kg of each nanomaterial type, on the level of a pilot plant, assuming the lower values for the various inputs and outputs, i.e. representing the maximum reduction potential (the absolute values behind this Figure can be found in Section 4 of the supporting information). This Figure shows a dramatic change in the relative contribution of the various elements to each impact category compared to the

results of the lab scale study (shown in Figure 3). In the case of such a (theoretical) pilot plant, the greatest impacts are caused by the production of the various starting materials (i.e. cobalt chloride, lithium methoxide, phosphoric acid, manganese acetate, and lithium hydroxide – combined, representing >60% of total impacts) and, in case of LMP, direct emissions to air and water (contributing up to 80% of the total impacts). The contribution of electricity consumption is still visible for most impact categories, but it is much lower compared to lab-scale production. The consumption of solvents and inert gas, which represented an important impact at the lab scale, are reduced considerably for the pilot plant; in particular, for nano-structured LCO their contributions are hardly visible anymore.

When investigating the influence of the key elements – i.e. the amount of input materials, inert gas, solvents and electricity for the (theoretical) pilot production – by changing from the lower to the higher value, the resulting impacts due to the production of 1 kg of these nanomaterials changes as shown in Figure 5.
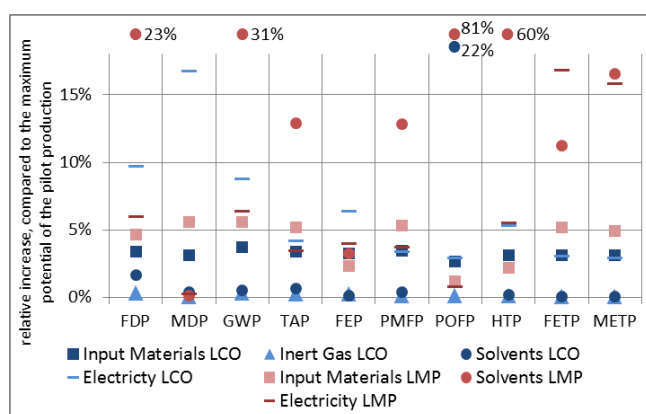
materials shows a more or less equal influence along the here investigated indicators in the order of 5%.

Figure 6 shows the degree of reduction of the total impacts of the (theoretical) pilot plant compared to lab-scale production, taking into account all the low and high values for the various elements (i.e. material input, inert gas, solvents, electricity) as described above (and listed in details in Chapter 2 of the supporting information). The results represent the range between the use of these low and high values respectively. Due to the fact that a second chemical product (i.e. LiCl) is produced in the here examined production pathway for LCO, the efforts from this process can be spread among these two products – i.e. they can be allocated. In order to investigate the influence of this additional factor, three different allocation principles have been applied: (a) all burdens allocated to $LiCoO_2$ (similar as for the lab-scale), (b) a split according to the prices of the two produced substances (LCO and LiCl) and (c) a split according to the mass amount of these two produced substances.
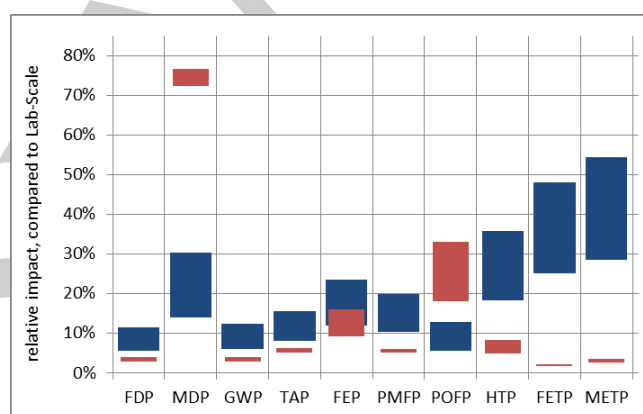

Figure 5. Relative changes of the environmental impact of the pilot production processes for LCO and LMP nanomaterials when changing the various key elements from the lower to the higher value. Shown are the same impact categories as in Figure 2.

Figure 6. Relative environmental impact ranges of the pilot production processes for LCO and LMP nanomaterials in comparison to the respective lab-scale impacts (set each time 100%). Shown are the same impact categories as in Figure 2.

Most of these investigated changes from the lower to the higher input values influence the impacts of the two nanomaterials to 5% or even less; especially inert gas and solvents in case of the LCO show hardly any influence with one exception: the POFP indicator shows an increase of the overall impact of more than 20% when doubling the amount of lost solvents. Otherwise, the result for LCO shows for a majority of the investigated indicators the highest changes in case of a variation of the electricity input, being responsible of increases of the total impacts of 3% (e.g. for POFP) up to 17% (for MDP). A change of the amount of the various input materials (representing actually a reduction of the yield of the whole process) shows a more or less equal influence for all here investigated indicators around 3 to 3.5%.

The result for LMP are most influenced by the amount of the various solvents – resulting in an increase of the impacts of the investigated (theoretical) pilot plant of up to 80% due to the assumed doubling of the amount of lost solvents. The electricity consumption results for most factors in an increase of around 4 to 5%, exception are the two ecotoxicity factors (FETP, METP) with an increase of more than 15% due to the higher electricity consumption. Again, a change of the amount of the various input

The latter of these three allocation principles results in a about 45% lower impact for LCO compared with the first principle, where all impacts are allocated to this nanomaterial. Therefore, combining this influence of the allocation principles with the ranges for the various input values (from low to high) lead then for LCO to a much broader variety of the results than for LMP with one exception – in case of the POFP indicator the high influence of the amount of solvents (see Figure 5) results for LMP in a two times higher variability than LCO shows despite the different allocation factors.

The MDP indicator in the case of LMP is the only impact category that shows less than 50% of reduction. This is due to the fact that the Co and Mn resources (being part of the starting materials cobalt chloride and manganese acetate for the investigated production pathways) have high impact factors in the calculation of this indicator. The four indicators FDP, GWP, TAP and PMFP, indicators that are broadly linked to the use of fossil resources (i.e. FDP and GWP) and/or emissions to air (i.e. GWP, TAP and PMFP), show a rather similar pattern for both materials. The value of the LMP pathway are around 20 times lower than that on the lab-scale level and are hardly affected by

the variations applied between the low and the high level options. In case of LCO, reduction is less and variation – mainly due to allocation issue – higher, but they represent still all in minimum 80 to 85% of reduction. This high reduction is a combined effect of reduced energy consumption and solvent usage, responsible for most of the emissions to air. As soon as at least one of these effects is not so distinct, the reduction potential from the lab-scale to the pilot production diminishes considerably, resulting in particular for LCO in a much higher range between the highest and the lowest value. Especially the toxicity impact categories HTP, FETP and METP show such a pattern in case of LCO; but despite this, all of them still show a reduction of at least a factor of 2, ranging in most cases to about a factor of 5. Common to all these impact categories is the fact that the variance is much higher compared to the variance for FDP, GWP and TAP. The LMP pathway shows here clearly higher reduction potentials and almost no variability (especially for the ecotoxicity factors) due to the fact that these impacts result – again – mainly from solvents and/or electricity consumption.

Comparison with other cathode materials

In order to evaluate the sustainability potential of the two new cathode materials, the LCA results of the above described pilot production (using the lower values from the (theoretical) pilot plant – in order to evaluate the full potential of these materials) are compared with those for various types of conventional cathode materials currently applied in Li-ion batteries: HT-LCO (the high-temperature method for the production of lithium cobalt oxide, $LiCoO_2$), LFP (lithium iron phosphate, $LiFePO_4$), LMO (lithium manganese oxide, $LiMn_2O_4$), and Li-NMC (lithium nickel manganese cobalt oxide, $LiNi_{0.4}Mn_{0.4}Co_{0.2}O_2$). The LCI data of these cathode materials were taken from publications by Notter and co-workers (for LMO), Majeau-Bettez and co-workers (for LFP and Li-NMC), and Dunn and co-workers (for HT-LCO).[21-23] These datasets were integrated into the here used LCA software tool and database (see experimental section). A first comparison of the impacts from the production of 1 kg of each of these materials is shown in Figure 7 (for absolute values, see Section 4 of the supporting information).
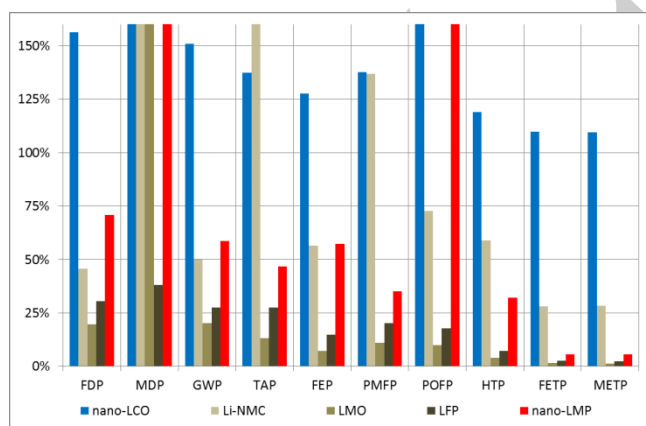

Figure 7. Relative Environmental impacts for the production of 1 kg of various Li-containing cathode materials, using HT-LCO (i.e. high-temperature lithium cobalt oxide) as measurement unit (i.e. HT-LCO is set as 100%). Shown are LMO = lithium manganese oxide, LFP = lithium iron phosphate, Li-NMC = lithium nickel-managese cobalt oxide as well as the two here examined nanomaterials for the same impact categories as in Figure 2.

Figure 7 shows a comparison of environmental impacts relative to those for HT-LCO (set as 100% for each of the examined environmental indicator). LMP nanomaterials shows for most of the examined impact categories a significantly lower impact than both forms of LCO, commercial HT-LCO and the here investigated, new nano-form. Exceptions with higher values for LMP are for photochemical oxidation formation potential (POFP), due to hexane releases into the atmosphere (responsible for almost 70% of this impact), and the metal resource depletion potential (MDP), due to the manganese content of the materials.

Compared to HT-LCO, the here modelled (theoretical) pilot production of LMP shows impacts being lower by a factor of 2 to 3. The LCO nanomaterial on the other hand doesn't show the expected advantages compared to the high temperature option based on the pilot process. However, different cathode materials result in Li-ion batteries with very different characteristics due to their differences in the capacity (Ah/kg and Ah/l), the midpoint voltage rates (in V vs. Li) and the resulting energy density (expressed in Wh/kg or Wh/l), as well as the stability (number of cycles that such a battery can be recharged) of the different materials. Hence, as battery performance is not considered, a comparison using a functional unit of 1 kg of Li-containing cathode materials is an inadequate means of designating the most "sustainable" cathode material. Typical values for key characteristics of the examined cathode materials are summarized in Table 1.

Table 1. Key characteristics of the various cathode materials examined in this study.

	nano-LCO	HT-LCO	LMO	Li-NMC	LFP	nano-LMP
Specific capacity [a]	175	140	110	165	160	153
Midpoint voltage [b]	3.9	3.9	4.0	3.8	3.4	4.1
Energy density [c]	683	546	440	627	544	628
average lifespan [d]	750	750	500	1500	1500	1500
Data Source(s)	see text	[24-28]	[24-28]	[24-28]	[24-28]	see text

[a] values in mAh/g. [b] values represent voltage vs. Li in V. [c] values in Wh/kg, calculated from the specific capacity and the midpoint voltage values. [d] values represent average number of cycles of the here examined materials, when used in Li-Ion batteries with graphite anodes. [e] see text.

The values for the commercial cathode materials have been taken from recent publications, representing typical values for these materials, while those for the two here developed nanomaterials have been derived by the authors, based on experiments and further assumptions. In detail, the following considerations are behind the values for the here examined, new materials:

• **nano-LCO**: According to experimental measurements of these authors, the capacity is 25% higher than for HT-LCO.[9] For the energy density the value was calculated out of this specific capacity by using a value for the potential of 3.9 V[9] and the number of charging cycles was assumed to be similar as for HT-LCO;

- **nano-LMP**: Regarding capacity, 90% of the value achieved by making nanoparticles of LMP and ball milling reported in Kwon and co-workers was assumed[11]; the value for the energy density was calculated from this by applying a value for the potential of 4.1 V.[11,14] For the number of charging cycles, the same value as for LFP were used, since both of these materials have a similar olivine structure.

To establish an alternative basis for comparing the various cathode materials is required; shown in Figure 8. Here, energy content (upper diagram; results per kWh of the totally stored energy over the indicated, average number of cycles) and capacity (lower diagram; results per Ah of the total capacity over the indicated, average number of cycles) were used as such a basis.
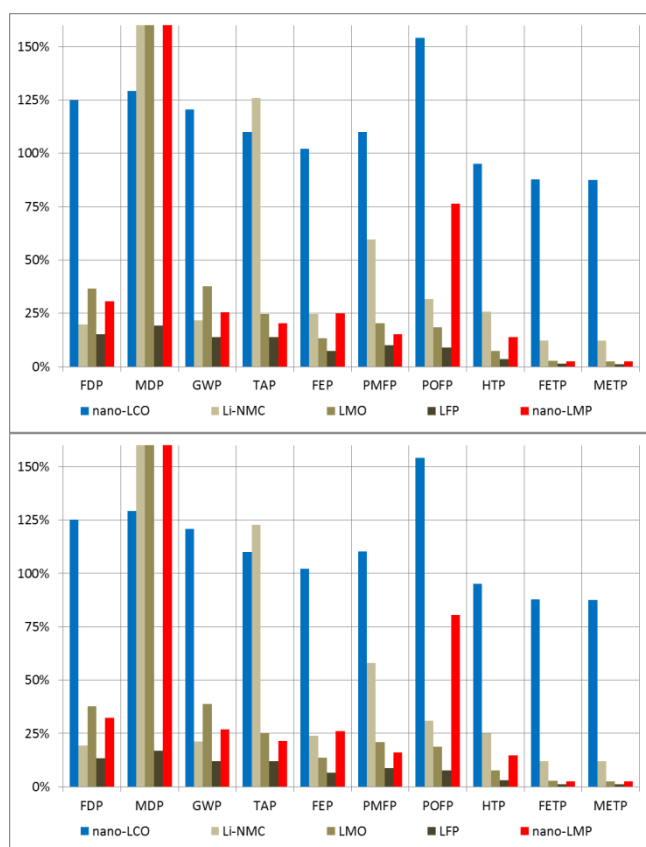

Figure 8. Relative Environmental impacts for 1 kWh of stored energy (upper diagram), and 1 Ah of available capacity (lower diagram), respectively, of the various Li-containing cathode materials, using HT-LCO as measurement unit (i.e. set as 100%); for the abbreviations of the materials see Figure 6. Shown are the same impact categories as in Figure 2.

The patterns of these diagrams show a more or less similar picture, and they are also partly similar to the pattern shown in Figure 7, i.e. on a per kg basis. Concerning the comparison based on energy content and capacity the only material for which results are at least partially higher than those of HT-LCO is the nano-form of the same material (i.e. nano-LCO). All other materials, including nano-LMP, show, for most of the examined impact categories, values that are factors lower than those for HT-LCO. For the category MDP, the results are still dominated by the contributions of manganese – which has a high

characterization factor – leading to results of up to two orders of magnitude higher for Mn-containing types of cathodes. Secondly, for POFP impacts nano-LMP had a much lower reduction (around 25%) due to hexane releases in the modelled production process. For all the other factors, the impacts from the here modelled pilot-scale nano-LMP are around a factor of 4 to 5 smaller than the respective impacts from the HT-LCO – being often in the same order of magnitude as the results for LMO – while LFP shows again lower results.

Discussion and Conclusion

Synthesis of Nano-LCO. To date, oxide materials for cathodes have been made using solid state, spray drying or, for more advanced oxides, co-precipitation methods[10]. These represent the simplest methods of mass producing these types of materials. By comparison, the organometallic approach described here has several advantages, most notably reductions in temperature and time requirements for producing the desired phase of $LiCoO_2$ (taking into account the annealing steps that are typically required for oxides). Furthermore, low temperature synthesis reduces particles growth and thus enables the production of more desirable nano-sized particles. Due to the resultant shorter path length of lithium ions, this results in faster lithium ion diffusion (i.e. faster discharge/charge time). Furthermore, as the reaction is almost instantaneous, low temperature synthesis of nano-$LiCoO_2$ is a relatively fast, straightforward process and produces a high overall yield of 80-95%. However, the process does require the use of much more expensive precursors than those used in the common synthesis route (i.e. oxides and carbonates). For the modelled pilot plant, it can be observed that the main contributors to the environmental impacts are the production efforts of all the raw materials themselves. Hence, to improve the overall sustainability of LCO-based Li-ion batteries it is of utmost importance that an alternative source of cobalt than cobalt chloride is found.

Synthesis of nano-LMP. It is known that wet chemistry often results in the formation of nanoparticles due to its homogeneous and stoichiometric reactions taking place at relatively low temperature[14]. However, yields from such synthetic methods are typically extremely low due to low concentrations in the solution. One advantage of the here described synthesis of $LiMnPO_4$ nanomaterials is, through appropriate selection of adequate surfactants and starting materials, its comparatively higher yields and ability to better control nanoparticle shape (rod, sphere, cubic, needle)[11,14]. As all subsequent electrode production and assembly processes were adopted from commonly used methods, they can be considered as being convenient for industrial upscaling as they require no major changes to existing procedures and processes. On the other hand, using surfactants and organic solvents increases environmental impacts and costs, although we expect that these can be reduced by through recycling of the organic solvents.

Sustainability potential analysis. The comparative LCA of the here investigated new nanomaterials (i.e. nano-LCO and nano-LMP) with conventional, commercial cathode materials shows that the potentials of the two new nanomaterials are quite different. While the modelled pilot production of nano-LMP

results in impacts that are in the range of those of the commercial materials, the results from the upscaling for nano-LCO do not lead to lower impacts. Rather, the chief contributors to the environmental impacts for the theoretical pilot production processes for both nanomaterials were found to be the starting materials and, albeit it to a much lower extent, energy consumption during the synthesis process. In particular, the starting materials clearly dominate the impacts from the production of nano-LCO, being responsible for over 80% of the total impacts for all impact categories. A a similar result is observed for manganese acetate, one of the starting materials for the production of nano-LMP, with it being responsible for 30-50% of total impacts. Further investigation into the effect of using alternative starting materials, if such materials can be found, on the sustainability potential of the materials is therefore required[18].

Further work is also required to obtain the technical measurements of the new cathode materials, while their development is expected to continue through, for example, their being applied in actual battery compositions. Regarding the sustainability potential analysis, the approach and results presented are currently limited to and valid only for the cathode materials considered. If possible to achieve, eventual increases in energy storage capacity (per kg and/or m^3 of battery) or battery life time would further add to the (ecological) advantages and sustainability of these new, alternative materials compared to conventional, commercial materials. Hence, the LCA analysis should be repeated after prototype Li-ion batteries that incorporate these new materials have been developed and tested. In particular, our analysis suggests that the nano-LMP shows considerable promise from a technical and sustainability perspective that warrants further investigation.

Acknowledgements

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